

REMOTE DETECTION OF POLLUTION OF WATER RESERVOIRS
AND PHYTOPLANKTON BY OPTICAL METHODS

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(NASA-TT-F-14767) REMOTE DETECTION OF
POLLUTION OF WATER RESERVOIRS AND
PHYTOPLANKTON BY OPTICAL METHODS (Kanner
(Leo) Associates) 20 p HC \$4.00

N74-19970

Unclass

CSSL 08H G3/13 33679

Translation of "Distantstionnoye obnaruzheniye zagryazneniye
vodnykh basseynov i fitoplanktona opticheskimi metodami,"
Vodnye Resursy, No. 3, 1972, pp. 65-74

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, DC 20546 MARCH 1974

STANDARD TITLE PAGE

1. Report No. 14,767 XXXXXXXX NASA TT F-	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle REMOTE DETECTION OF POLLUTION OF WATER RESERVOIRS AND PHYTO-PLANKTON BY OPTICAL METHODS		5. Report Date March 1974	
		6. Performing Organization Code	
7. Author(s) K.Ya. Kondrat'yev, A.A. Buznikov, and D.V. Pozdnyakov Leningrad State University		8. Performing Organization Report No.	
		10. Work Unit No.	
9. Performing Organization Name and Address Leo Kanner Associates, P.O. Box 5187, Redwood City, California 94063		11. Contract or Grant No. NASW-2481	
		13. Type of Report and Period Covered Translation	
12. Sponsoring Agency Name and Address NASA Washington, DC		14. Sponsoring Agency Code	
15. Supplementary Notes Translation of "Distantstionnoye obnaruzheniye zagryazneniy vodnykh basseynov i fitoplanktona opticheskimi metodami," Vodnye Resursy, No. 3, 1972, pp. 65-74.			
16. Abstract A report on the remote detection of polluted water surfaces and phytoplankton by optical methods, for which there is a great need at the present time, owing to the large amount of oil spilled from tankers, etc. The most promising method is to take advantage of the physical properties of the substances being investigated which contrast with those same properties of clean water. An example is the rise of temperature contrast when oil is present on a water surface. However, much laboratory research into the optical properties of various oils and petroleum products must be done and the results catalogued. In every case, the intermediate mass of the atmosphere must be taken into account when researching into pollution detection.			
17. Key Words (Selected by Author(s))		18. Distribution Statement Unclassified - Unlimited	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 1820	22. Price 4.00

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REMOTE DETECTION OF POLLUTION OF WATER RESERVOIRS
AND PHYTOPLANKTON BY OPTICAL METHODS

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One of the consequences of the ever-growing amount of present- /65*
day industrial production is the progressive pollution of the
Earth's water reservoirs. The most serious sources of pollution
are the dumping of industrial waste and discharge of oil and
petroleum products. The scale of water pollution by oil has
already become quite considerable [13]. The most serious pollution
arises as the result of insignificant, in each concrete case, but
exceedingly numerous losses of oil products by vessels and tankers
when refueling, unloading, cleaning and other practical operations.
Apart from this, as a result of heavy damage of various kinds and
shipwrecks, approximately 1,000,000 tons of oil are discharged into
seas and oceans each year. One very serious source of pollution
can sometimes be oil wells at sea. Hence during the gushing of a
well in the Santa Barbara channel (Southern California) in 1959,
approximately 500,000 tons of crude oil were discharged. Oil is
being spilled over large areas of water surfaces and is a serious
threat to the biosphere on account of its toxicity.

The results of dumping into rivers, lakes and other reservoirs
of untreated water, which contains chemical active substances (for
example, nitrogen compounds) is stimulating the reproduction of
phytoplankton. Excessive content of the latter in slow-flowing
reservoirs brings about a depletion of their waters with dissolved
oxygen and the gradual death of underwater forms of life. At the
present time, apparently, no exact figures are known which show
the extent of this type of pollution, however the problem is
obviously a serious one.

*Numbers in the margin indicate pagination in the foreign text.

The last few years have been characterized by intensive search for finding a method for preserving water resources. Active biological inhibitors are being developed, which slow down the reproduction of phytoplankton, CaCO_3 , polyurethane and dispersing agents for cleaning up the results of oil and petroleum product leakages are being used [13]. However, the efficiency of these measures, to a large extent, depends on whether they are used in good time. In this regard, the development of methods and means for the detection and localization of this type of pollution on water is becoming more important.

It must be recognized that remote aerial and space (satellite) methods are most promising. In these methods they rely on the use of one or another physical properties of objects undergoing research, which form a contrast with the similar properties of a pure water surface.

The present review is devoted to the study of possibilities for using optical characteristics of the system: oil-water and phytoplankton-water for the remote detection of pollution and phytoplankton. Let us note that the problem of phytoplankton in seas and oceans is of interest in a completely different aspect /66 than shown above. The evaluation of content of phytoplankton in seawater is very important when looking for shoals of fish in areas where there is an intense phytoplankton production [2].

The basic properties of surface layers of polluted reservoirs. Experimental tests have shown [9] that, when there are large spillages of oil on a water surface, at first a layer is formed approximately 2 cm thick, which afterwards gradually spreads to a film (10-100) μm , the thickness of which is determined by the equilibrium of the oil on the surface of the water

$$F = \gamma_w - \gamma_o - \gamma_{o/w},$$

where F is the strength of oil spread, γ_w is the surface tension of the water, γ_o is the surface tension of the oil, $\gamma_{o/w}$ is the surface tension on the boundary division of oil-water.

As the oil spreads, its composition becomes considerably changed. As is known, oil is a complex organic compound, containing unsaturated, aliphatic and aromatic hydrocarbons. When it comes into contact with the water, the toxic substances, which in oil are mainly aromatic hydrocarbons, dissolve, and the light fractions of unsaturated hydrocarbons evaporate. The remaining components are also changed: depending on the properties of the underlying water (salinity, temperature, the presence of microorganisms and dissolved chemically active substances, and also atmospheric conditions) they can undergo auto-oxidation, photochemical oxidation (from the effect of ultraviolet solar radiation in the range 3100-4000 Å), biochemical oxidation (by sea microorganisms) and polymerization (when corresponding dissolved catalysts are present in the water). As a result of these processes, and also due to the intense natural agitation of the waves, after a certain time, an ~80% aqueous emulsion made up of heavy fractions, covered by a flaked-off resinous film, forms on the surface of the water [13].

The appearance on the water surface of an oil layer changes the thermodynamic equilibrium in that part and causes the occurrence of a temperature contrast. The nature of this contrast is quite complex and is determined by several factors.

First of all, the oil layer, preventing the formation of capillary waves and suppressing high-frequency waves, to a considerable extent reduces the rate of evaporation from the water surface, and this leads to a rise in temperature. On the other hand, the surface of the water, covered by oil, has a higher

reflection coefficient [8] and, according to Kirchhoff's¹ law, must have a lower radiating capacity. Hence, in the 10 μm range, the radiating capacity of water $\epsilon_w = 0.993$, and on the boundary of oil-water, $\epsilon_{ow} = 0.972$ [9] and its radiation temperature must be lower (in theoretical calculations it is approximately 1°C lower [9]) than the temperature of the surrounding water. Finally, since in the system reviewed, the molecular mechanism of heat exchange through the boundary limit has a decisive value and prevails over convective and turbulent mechanisms [9], one must take into account that the thermal conductivity of oil and petroleum products is less than that of water in approximately 1/67 the same amount. Taking these factors into consideration, it must be expected that the temperature contrast must depend significantly on the thickness of the oil layer. The thermal contrast between polluted and clean expanses of reservoirs opens up possibilities for using infrared images to trace the characteristics of polluted areas.

Apart from the thermal anomaly, pollution areas have optical features which can be used as a contrast for remote detection of them. Since these features have significant selectivity, let us look at the optical properties of pure and polluted water in various sections of the electromagnetic spectrum.

As is already known [6], in close ultraviolet and visible ranges of the spectrum, water is transparent to solar rays. Its true color is determined by the dispersion of light rays on molecules of water and small suspended particles. The wavelength of the maximum dispersed light fluctuates considerably: for pure water in the ocean $\lambda_{\text{max p.}} = 470 \text{ nm}$ and for pure coastal water,

¹In fact, since an oil film is semi-transparent to heat rays, the ratio for Kirchhoff's "radiating capacity equal to one unit minus the reflective capacity," prescribed for opaque bodies, must be replaced by the MacMahon formula [9].

550 nm. In this regard, the purest ocean water is of a dark-light-blue color, and the coastal areas of seas and oceans are normally greenish. If, however, there is an estuary on the coast, the color of water can be red or brownish, depending on the polluted waters discharged into it [19]. In natural conditions, the color of water depends on the spectral composition of radiation deflected from its surface and, in this way, to a certain degree, takes its color from the color of the sky.

In close ultraviolet and visible ranges of the spectrum, the refractive index of pure water is $n \approx 1.3$ and, consequently, the Brewster angle equals 53° , that is, light, reflected at this angle, is plane polarized. The general characteristic of the spectral curve of reflection from the surface of pure water is of an evenly decreasing character [6], with small maxima in the maximum natural dispersion range (Fig. 1, a).

When an oil film with a thickness of not less than several tenths of mono-layers falls onto the surface of water, the optical properties of this system in the reviewed range of wavelengths differs from the optical properties of pure water [8]. As has already been mentioned, there are light and heavy fractions in the composition of oil. Research has shown [16] that when there are moderate illumination densities, caused by electron transitions, the lighter fractions are absorbed into the longwave band of approximately 300 nm, and the heavier fractions, into the longer-wave band of the spectrum -- 370 nm (Fig. 1, b). It is known [11] that in certain conditions, the indicated electron transitions can cause fluorescence. Here, luminescent spectra of light and heavy fractions are different. Light fractions fluoresce at 360-460 nm, and heavy fractions at 520 nm. When the oil layer is illuminated by a laser beam, which is characterized with its extremely high density of its monochromatic beam, electron transmissions are possible, which correspond to a very high quantum output of fluorescence [12].

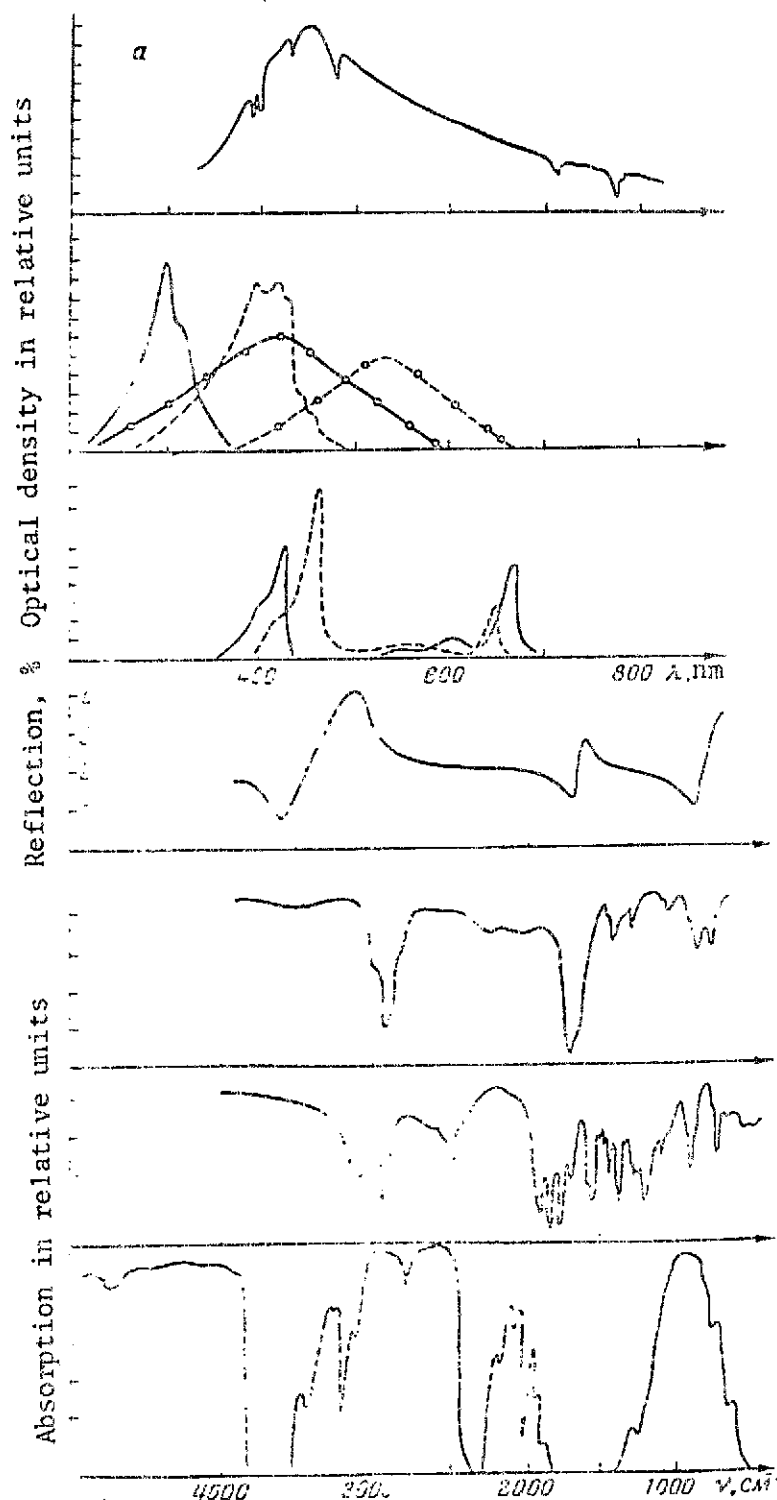


Fig. 1. Some spectral characteristics of water, oil and chlorophyll in the optical longwave band: a - spectrum of radiation dispersed with water; b - spectra of agitated light (—) and heavy (-o-) fractions of oil, and also spectra of luminescence of light (---) and heavy (-c-) fractions of oil; c - agitation and luminescent [continued on following page]

Fig. 1, cont'd: spectra of chlorophyll a (—) and c (---);
d - spectra of reflection from the water surface; e - absorption
spectrum of heavy fractions of oil; f - absorption spectrum of
chlorophyll; g - absorption spectrum of the atmosphere at sea level.

Since the refractive index of oil in the reviewed spectrum range is $n \approx 1.6$ [16] and, consequently, higher than water, then, firstly, outside of the natural absorption bands, the oil film, when beams fall on it at narrow angles, must reflect better than water and, secondly, the Brewster angle in this case is 58° .

In this way, in ultraviolet and visible ranges of the spectrum, the oil film - water system has dispersion and reflection spectra which differ from those of water (on account of the natural absorption bands of oil); in certain conditions it can fluoresce and, finally, have another Brewster angle.

In the close infrared range (up to $15 \mu\text{m}$, i.e. 660 cm^{-1}) water is a heavy absorber of beams, and its spectrum is characterized by a series of absorption bands, which could undergo basic and overtone fluctuation transitions. The reflection spectrum of water (Fig. 1, d) has several bands, lying close to its absorption band. It has been ascertained [12] that when salts containing anion CO_3^{2-} , SO_4^{2-} and Cl^- are present in concentrations characteristic of seawater, the reflection spectrum does not change. If the concentrations of these salts are abnormally high, additional bands in the $1300\text{--}1000 \text{ cm}^{-1}$ ($7.7\text{--}10 \mu\text{m}$) appear in the spectrum. The reflective power of a water surface in the close infrared range does not exceed 4%, the refractive index (outside of the absorption bands) is approximately 1.3, that is, the Brewster angle equals approximately 53° .

The absorption spectrum of oil in the range $1\text{--}15 \mu\text{m}$ is characterized by a group of absorption bands, which can undergo fluctuating transitions, belonging to various structural groups,

in one amount or another present in the composition of both light and heavy fractions (see Fig. 1, e). The refractive index of oil is higher than the refractive index of water and, consequently, in the infrared range, one must expect higher values of reflection coefficient from a surface covered by oil (outside of the natural absorption bands of oil) [9]. As calculation has shown [8], the reflection during normal incidence, in this case, can be increased by approximately 20%.

In this way, apart from the temperature contrast, in the infrared range of the spectrum, the differences in values of the reflection coefficient and the polarized characteristics (Brewster angles) can be used as contrasts. It is convenient to make a comparison of the reflection from the surface of water and the oil-water with respect to the transmission of the atmosphere (Fig. 1, g) in the following ranges of the spectrum (at low observation heights, these ranges can be significantly enlarged): $4800-4000\text{ cm}^{-1}$ ($2.08-2.5\text{ }\mu\text{m}$), $2700-2500\text{ cm}^{-1}$ ($3.75-4\text{ }\mu\text{m}$) and 1000 cm^{-1} ($10\text{ }\mu\text{m}$).

As is known, the optical characteristics of phytoplankton are closely linked with the optical properties of chlorophyll, which is a complex, metallo-organic compound [1]. In the visible range of the spectrum, chlorophyll absorbs at wavelengths of 420-460 nm (an electron transition $S_0 - S^*$) and 640-680 nm (electron transition $S_0 - T$) (Fig. 1, c). In certain conditions, the transition of electrons can be fluoresced [1], when the fluorescence mechanism can be ambiguous and is characterized by diagrams shown in Fig. 2.

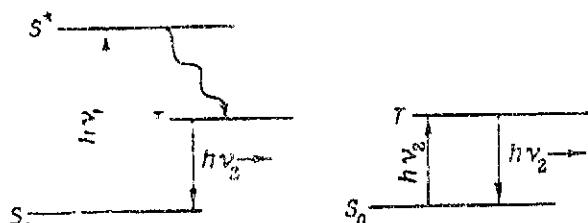


Fig. 2. Diagrams of two stimulation and luminescence mechanisms of chlorophyll.

Although the maximum of fluorescence, as can be seen from the diagrams, is situated in both cases in the 640-680 nm band in the

energy ratio, the first fluorescence mechanism is preferable for remote indication, since it is characterized by a considerably higher quantum output of fluorescence than in the second case. In the close infrared range of the spectrum, chlorophyll is transparent. In the longer-wave range absorption bands appear in the spectrum, which can result in fluctuating transitions, belonging to various structure groups (see Fig. 1, f). As can be seen, the spectrum of chlorophyll in the infrared range is complex and it is difficult to use it for indication.

In this way, the chlorophyll-water system has the following features: the phytoplankton changes (because of the natural absorption bands at 420-460 nm, that is, in a range approaching the maximum of light dispersion by water) the spectrum, leading to a sharp quenching of the light-blue range and a shift of maximum intensity to a wavelength of ~ 550 nm, that is, into the green range. Apart from this, under certain conditions, the system can fluoresce with maximum radiation at 640-680 nm (in the red range of the spectrum).

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Examples of practical realization of remote methods of spectral detection. At the present time, there is a considerable number of works in which are described: attempts for practical realization of methods for spectral, remote detection of oil spillages and colonies of phytoplankton [9-11, 15-18]. Some of these are discussed in the review [2].

The majority of work published is based on the use of aerial measurement data, although the first experiment in space indication took place onboard the "Soyuz-9" manned spacecraft [3]. In this experiment spectral photometry of a number of natural formations was carried out, including water surfaces, by using a spectrograph with a diffraction grating (a resolution of approximately 5 nm), operating in the 400-700 nm range. From a height of 250 km a surface section with an area of $8 \times 0.45 \text{ km}^2$ fell across the field

of vision of the instrument. The spectra obtained of the intensity of light dispersed by water of lakes of the Mesopotamian lowland, of southwest Afghanistan, and also of the Aral Sea a maximum of 550 nm was observed, which shows that vegetation was present in this water (Fig. 3). Relatively higher values of the brightness coefficient in the 400-500 nm range, in comparison with values of this coefficient at the level of the underlying surface, are linked with the effect of atmospheric haze [3-5].

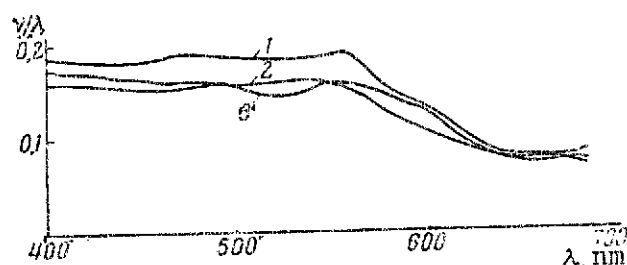


Fig. 3. Spectral brightness coefficients of some reservoirs, obtained from the manned spacecraft "Soyuz-9": 1 - lakes of the Mesopotamian lowland; 2 - lakes of southwest Afghanistan; 3 - the Aral sea.

G. Clarke et al. [10] give reports on research into the surface of water containing phytoplankton, by using an aircraft spectrograph, working in the 400-700 nm longwave band and having a resolution of 5-7.5 nm. The instru-

ment had a field of vision of $3 \times 0.5^\circ$ and from a height of 300 m covered an area of $16 \times 3 \text{ m}^2$. The authors only researched into light scattered by water [10], using the polarization effect of solar radiation reflected from water. The surface of the water was aligned at an angle of 53° , i.e., at the Brewster angle. The reflected radiation was plane polarized and was completely eliminated by using nicol. As a result, only the component scattered by water was recorded.

The spectra obtained confirmed the expected effects of quenching in the blue range (430 nm) and the shift of the intensity maximum of light scattered by water to 560 nm. Calibration of the instrument [10], carried out on a gray Kodak screen, made it possible to evaluate the sensitivity of the method: the instrument

gave a definite registration of the presence of chlorophyll in water when its concentration exceeded 0.3 mg/m^3 .

D. Arvesen et al. [7] carried out remote indication of phytoplankton from a height of 150 m, by measuring the radiation (scattered and back-scattered) in the 380-1000 nm longwave band. /71 The resolution of the spectrometer (due to its double monochromatization) was on the order of 1 nm. The spectra obtained contained a distinct absorption band, characteristic of chlorophyll. Apart from the spectrometer, they used a differential radiometer with filters, making it possible to compare the radiation intensity in the $\lambda = 443 \text{ nm}$ wavelengths (the absorption band of chlorophyll) and 525 nm (outside of the chlorophyll absorption band). Comparison of data obtained by using the differential radiometer, with data from the direct measurement of chlorophyll content, showed there was a linear relation of radiometer readings to the logarithm of chlorophyll concentration. The presence of such a sensitive correlation made it possible to trace continuously the concentrations of chlorophyll along the flight path in the concentration ranges from 0.03 to 10 mg/m^3 and greater. Measurements with an infrared radiometer (calibrated on an internal source -- a tungsten lamp with a halogen filler) showed, in several instances, a definite negative correlation between the chlorophyll concentration in the surface layer of water and the temperature of that layer.

Apart from passive method for sounding phytoplankton, active methods are being developed, which depend less upon meteorological conditions and make it possible to make observations at any time of the day. Hence, A. Measures [15], using the luminescence effect of chlorophyll, constructed an aircraft instrument based on a powerful laser radiating at $\lambda = 650 \text{ nm}$. Although first measurements showed the validity of this method, the sensitivity of the instrument, was not high. Further, some authors propose using laser radiation with $\lambda = 420-440 \text{ nm}$, i.e., in the absorption range band of chlorophyll, the quantum fluorescence output of which is considerably higher than for the 680 nm band.

Works [9, 11, 13, 16-18] are devoted to the remote indication of oil spills on the surface of water. D. Millard [16], for example, used the set of aircraft instruments described above to do this. A certain amount of known types of oil was discharged into the sea and observations were carried out during the first 3 days. Only 3 hours after the moment when the oil had been discharged, the thickness of its film on the surface of the water was approximately 20 μm . Measurement was done in the 380-950 nm long-wave band, by using a spectroradiometer (with a resolution on the order of 3-6 nm) and a differential radiometer. The field of vision was approximately 10° when observations were carried out in a vertically downwards direction. Data obtained by the spectroradiometer showed that when there was a large amount of cloud, the oil film was 70% brighter than the surface of the water /72 (comparison was carried out on a 400 nm wavelength). The authors came to the conclusion that in the visible range of the spectrum, the maximum contrast on the background of a clear water surface is given by lighter types of petroleum products. Apart from this, it was noticed that the most favorable observation conditions take place when there is complete cloud cover (see below). The spectral characteristic of contrast is such that its maximum is in the ultraviolet and red ranges of the spectrum, the minimum -- in the longwave band of maximum radiation scattered by water (450-500 nm).

Measurement with the differential radiometer was done in two operations. 1. A filter, with a radiotranslucency of approximately $\lambda = 526$ nm (the suggested fluorescence peak of heavy types of oil) was placed in one of the channels, and one with $\lambda = 576$ nm (outside of the fluorescence peak) was placed in the other. When flying was done over the pollution area being investigated, the difference in signals observed was 5%. A filter (for 380 nm) and a polaroid were placed in each of the channels; in one channel, the polaroid was oriented parallel to the flight path (in the Sun's plane), in the other, perpendicularly. The recorded difference in signals

during flights above the area of the oil film was approximately 25%.

On the basis of data obtained, the authors came to the conclusion that the most promising method is the polarization one, and the method based on the effect of natural fluorescence, apparently, is not of practical interest. However, works [11, 15] showed that the fluorescence method can be used successfully, if a powerful laser is used as an active locator. As was said above, laser radiation can cause the occurrence of new transitions with very high quantum fluorescent output.

H. Gross and A. Davis [11] researched into the luminescence of various types of petroleum products by using a helium-cadmium laser (of 50 mW power) with a reset wavelength. The authors observed that the spectrum of fluorescence of various types of oil and petroleum products differed and did not coincide with similar spectra, obtained when using nonlaser sources. Hence, one of the types of oil, when radiated by nonlaser sources, fluoresces at 530 nm, and when there is laser stimulation, there is a strong luminescence at 460 and 480 nm.

A. Measures et al. [15] attempted theoretically to substantiate the laser-sounding method for semitransparent layers. They showed that if a laser locator with a radiation power of P^1 is at a height of R , the luminescent flow in the $\Delta\lambda$ range, reaching the sensitive element of the instrument with a limiting aperture radius a , is determined by the ratio

$$S^r = \frac{C^r(\lambda) a^2 P_{\xi}^T(\lambda) \Delta\lambda}{R^2},$$

where $C^T(\lambda)$ is the function of the film thickness, the nuclear cross sections of fluorescence, the densities and coefficients of absorption of the film and the underlying surface, $\xi^T(\lambda)$ is the transmission factor of the intermediate mass of the atmosphere and the optical system of the instrument.

As can be seen from this formula, the "fluorescent method" is preferable for thick films. The authors [15] showed that for the laser which they used (3471 \AA), the power of luminescent radiation grew directly proportionally to the increase of thickness of the oil film from 0.1 to $10 \text{ }\mu\text{m}$. However, when the thickness of oil is greater than $10 \text{ }\mu\text{m}$, saturation was observed, due to absorption in the oil layer. It was noted that laser radiation with $\lambda = 3471 \text{ \AA}$ causes the fluorescence of water, the nature of which is not /73 completely clear, but there is basis to believe that it is connected with the effect of microorganisms. For this reason, it is preferable to use a laser with $\lambda = 4000 \text{ \AA}$, when there is no fluorescence of water and the contrast value is great. Knowing the noise threshold of the system and taking into account that $S^F \approx 1/R^2$, the authors [15] determined, in their case, the optimum height for sounding. It was 250 m (here, the requirements for speed of inspection of the given area were taken into account).

In work [9] there is information on the use of a thermal detector, working in the $8\text{-}14 \text{ }\mu\text{m}$ range, standard aerial cameras and spectral video systems, for detecting oil. The most effective was the thermal detector, which has a high space resolution and good sensitivity, is simple to manipulate and suitable for use at any time of the day. Thermal contrasts of oil spills detected by this instrument show that the peripheral parts of the spills, like the thinnest ones, are colder than the surrounding water. The highest temperatures were observed in the center of the spill, where the oil layer is at its thickest and where resinous agglomerates often accumulate.

The use of aerial camera films, sensitive to various parts of the spectrum, showed that in the $2800\text{-}4000 \text{ \AA}$ range, the oil film was quite contrasting to the background of water. Data on the relative contrast in the visible spectrum band are contradictory. Thus, in work [16] the maximum contrast was observed

for blue and red rays, but according to data by P. Chandler [9], the blue and red ranges, on the contrary, contained little information and the greatest contrast was observed in the violet range. Finally, according to data by D. Munday and others [18], maximum contrast for thick films was observed in the green range. This disparity of results, apparently, is explained by the strong relation of contrast to the thickness of the oil film (which could differ considerably in experiments by different authors) and observation conditions. The last fact, as was shown in a work by D. Millard and D. Arvensen [17], is very significant when observing oil films. Proceeding from the general considerations, the authors showed that the effects of polarization of incidence and back-scattered radiation limit the optimum sighting angle of the surface, which must be smaller than the Brewster angle. This is especially important when using the polarization technique when detecting pollution.

P. Chandler [9] tells how he used a microwave locator for remote detection of oil spills, which operated in the 3 and 19.35 GHz frequencies. The experiments showed that, in the microwave band, the film is always only observed as a positive thermal contrast. Stating that this type of active locator could work in any weather conditions and at any time of the day, the author also indicates the significant disadvantage of this method, which is the low space resolution and the complexity of processing the results.

Conclusion. Data reviewed above show that the problem of remote detection of oil films and phytoplankton can be solved principally by using optical methods. The urgent problems are to find the most effective method for such measurements and the development of corresponding equipment, suitable for operational use. The first steps in this direction have already been taken. However, many aspects of the problem require further development.

In order to solve the problem for detecting oil spills, careful laboratory research is required, on the basis of which a catalogue of the optical properties of various types of oil and petroleum products in various stages of change, to which they /74 are subjected in natural conditions, could be made.

Search must be carried out into the stable correlations between the thickness of an oil layer, its composition and optical contrast in different lighting conditions and the state of the sea surface. Here, attention must be paid to the effect of the intermediate mass of the atmosphere. The most important in this respect is work on determining the transfer function of the atmosphere [4, 5], which would make it possible to transform the spectral characteristics obtained from space or at the level of the underlying surface by high-flying aircraft.

In order to solve this problem, it is very important to carry out simultaneous complex measurements in various regions of the electromagnetic spectrum, the results of which would complement each other and also to carry out independent, direct measurement of the investigated parameters. Carrying out these measures would undoubtedly make it possible, in the near future, to develop effective, remote search methods and the characteristics of areas of polluted reservoirs.

It must be stressed that the functions of this type of method and equipment can be significantly enlarged by using them for detecting oil deposits (by the natural show of oil on the surface of the sea), and also for the search for shoals of fish (in areas where there is an increased concentration of phytoplankton).

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